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Patterned growth of single-walled carbon nanotube arrays from a vapor-deposited Fe catalyst

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Single-walled carbon nanotubes have been grown on a variety of substrates by chemical vapor deposition using low-coverage vacuum-deposited iron as a catalyst. Ordered arrays of suspended nanotubes ranging from submicron to several micron lengths have been obtained on Si, SiO₂, Al₂O₃, and Si₃N₄ substrates that were patterned on hundred nanometer length scales with a focused ion beam machine. Electric fields applied during nanotube growth allow the control of growth direction. Nanotube circuits have been constructed directly on contacting metal electrodes of Pt/Cr patterned with catalysts. Patterning with solid iron catalyst is compatible with modern semiconductor fabrication strategies and may contribute to the integration of nanotubes in complex device architectures. © 2003 American Institute of Physics. [DOI: 10.1063/1.1627935]

Carbon nanotubes have attracted intense attention in recent years due to their interesting physical properties and potential applications.^{1,2} The controlled growth of carbon nanotubes is critical in practical applications and a number of recent reports have addressed this issue.^{3–9} For example, Dai's group⁸ obtained suspended single-walled nanotubes (SWNTs) oriented parallel to the substrate surfaces on specific sites by a methane chemical vapor deposition (CVD) growth method. This method relies on liquid solutions containing catalyst nanoparticles, which are transferred to patterned substrate surfaces by contact printing. There are also reports of multiwalled carbon nanotube growth from vapor deposited solid catalyst films.^{4,5,9–11} However, little work has been done on directing the controlled growth of SWNTs on specific sites using solid catalyst films.¹² Here, we show that very low coverage of vapor-deposited Fe serves as a reliable catalyst for the growth of SWNTs. By patterning the Fe catalyst, we obtain ordered arrays of suspended SWNTs on predefined locations using a methane CVD growth method. Furthermore, locally applied, "on chip" electric fields¹³ were utilized to successfully manipulate the growth directions of SWNTs. Finally, device-quality SWNTs were grown directly on catalyzed metal electrodes with good electrical contact.

In our experiments, Fe was deposited by thermal evaporation in a vacuum of 10^{-6} Torr. The Fe coverage was typically 5×10^{15} atoms/cm² (corresponding to a few monolayers) as determined by Rutherford backscattering. Catalyst regions were patterned into arrays of small posts or parallel stripes of different dimensions by using a focused ion beam (FIB) machine (FEI Micrion 9500, 50 kV). Unless otherwise

specified in the letter, nanotubes were then grown in a quartz tube oven at a temperature of 900 °C in the flow of methane (1000 sccm) for 4–20 min.⁸ Heating up and cooling down were done in an argon flow. High-resolution scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the carbon nanotubes. For TEM imaging, multiple gaps or holes were ion beam etched all the way through self-supporting 0.5- μ m-thick Si₃N₄ membranes.¹⁴ The substrate then formed a natural electron microscope grid upon which nanotubes could be grown and studied by TEM directly.

Figures 1(a)–1(d) show the growth behavior of nanotubes on patterned Si₃N₄ membranes as observed with a SEM operated at 1 keV. Using such a low energy SEM allows direct observation of suspended nanotubes. The width of the Fe coated Si₃N₄ regions on different patterns ranged from 200 to 500 nm. These regions clearly serve as the initiation and termination sites in the nanotube growth process.

Figure 1(a) shows the nanotubes grown across 500 nm wide gaps. The growth time was 10 min in the methane flow. Most crossing nanotubes were grown in directions approximately perpendicular to the long gap direction. As the gap width is increased to 700 nm, 1.3, and 3 μ m [Figs. 1(b), 1(c), 1(d), respectively], the nanotube density decreases and the tubes that succeed in traversing the gap are more nearly aligned perpendicular to it. A likely explanation is that the Van der Waals' interaction between the thermally vibrating nanotubes¹³ and the substrate successfully returns most nanotubes to the substrate segment they start from, unless their initial growth direction is nearly perpendicular to the gap, or a tube–tube collision results in growth in that direction. Long suspended nanotubes can be easily obtained even for gaps exceeding 5 μ m. Near the edges, two or more tubes usually join together to form a long tube across the gaps. This demonstrates that interactions between the floating

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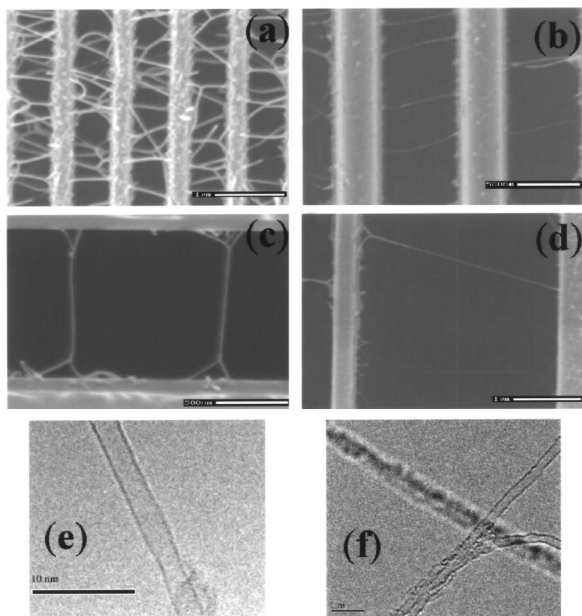


FIG. 1. SEM (a)–(d) and TEM (e), (f) images of nanotubes across parallel gaps etched through free-standing Si_3N_4 membranes. (a) 500 nm wide gaps with remaining stripes 300 nm wide. Scale bar: 1 μm . (b) Gaps 700 nm wide. Scale bar: 500 nm. (c) Gaps 1.3 μm wide. Scale bar: 500 nm. (d) Gaps 3 μm wide. Scale bar: 1 μm . (e) TEM image of a suspended individual SWNT. Scale bar: 10 nm. (f) From bottom left to top right: the split of a nanotube bundle into two individual SWNTs. From top left to bottom right: an out-of-focus image of another nanotube. Scale bar: 5 nm.

nanotubes during the growth process are important in forming nanotube structures.

TEM (200 kV) images were taken of suspended nanotubes grown across gaps on catalyst-coated Si_3N_4 membranes. In Fig. 1(e), the wall structure of an individual SWNT is clearly seen. Figure 1(f) shows the split of a two-tube bundle into two individual SWNTs 2 nm in diameter. Most of the nanotubes observed in our samples, even very long nanotubes, are isolated individual SWNTs, or bundles made of only a few SWNTs. The diameter of most SWNTs ranges from 1 to 4 nm from TEM studies. It has been suggested that nanometer-sized catalyst particles are required to seed nanotube growth.^{15–18} Gaseous carbon compounds presumably decompose on the surface of catalytic metal droplets, and carbon nanotube growth occurs by diffusion-driven precipitation of carbon from the supersaturated catalyst nanoparticles. For low coverage Fe depositions, nanoscale droplets nucleate at the surface during the high temperature treatment.^{10,11} From atomic force microscopy images taken on Fe deposited surfaces before and after annealing at 900 °C with argon flow, we clearly observe the aggregation of nanoparticles (ranging from nanometers to hundreds of nanometers) due to the heating process. Also, at both ends of the nanotubes observed by SEM, the size of nucleation sites is of order or less than the resolution of the SEM (~ 10 nm). Therefore, they possibly grow from 10 nm or smaller Fe particles.

We also studied the growth behavior of nanotubes on different substrates commonly encountered in semiconductor device fabrication, such as Si(111), Si(100), SiO_2 , and Al_2O_3 . Figure 2(a) shows nanotubes crossing trenches 700 nm wide on a Si substrate coated with insulating SiO_2 layer for a growth time of 20 min. In Fig. 2(b), suspended nano-

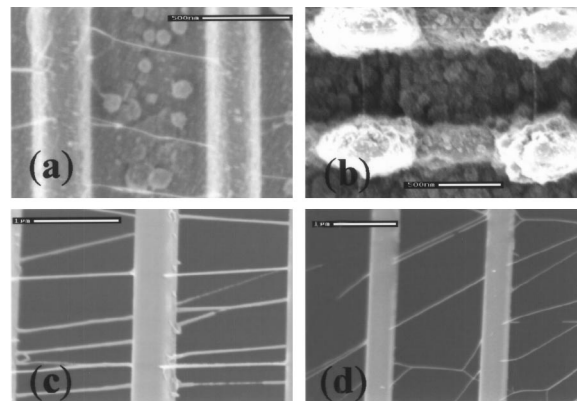


FIG. 2. SEM images of SWNTs connecting stripes or posts patterned on (a) a SiO_2 (5000 Å)/Si substrate (grains due to etching are seen in the bottom of the trenches. Scale bar: 500 nm) and (b) an Al_2O_3 (1000 Å)/Si substrate (Scale bar: 500 nm). (c) SEM images of SWNTs across gaps in Si_3N_4 membranes with 4 min growth time, under applied electric field perpendicular to the gaps (0.5 V/ μm) and (d) at a 45° angle relative to the gaps (2.4 V/ μm) (Scale bar: 1 μm).

tubes are connecting arrays of post on Al_2O_3 coated Si substrate.

So far, the directional alignment of nanotubes in our experiment is mainly determined by nanotube-substrate and nanotube–nanotube interactions and thermal vibrations, which make most of the nanotubes orient themselves roughly in a direction perpendicular to the gaps or trenches. To get better control in the growth of nanotubes we explored the utility of applying electric fields to align the nanotubes during the growth process.^{13,19} Here we show that locally applied electric fields are very effective in manipulating the growth direction of SWNTs from our Fe catalyzed surfaces. In our experimental setup, two 20 μm wide electrodes (Pt 40 nm/Ti 50 nm) spaced 10 μm apart end on, were patterned by optical lithography on self supported insulating Si_3N_4 membranes. The Fe catalyst was deposited in the space between the electrodes, and then that space was patterned into parallel gaps with the FIB. During the CVD growth process, a bias voltage was applied between the electrodes to generate an electric field in the gap areas. Figure 2(c) shows the result for a sample under a bias voltage of 5 V and 4 min growth time. The electric field direction was perpendicular to the gaps. Compared with the results without electric fields during growth, the nanotubes look straighter, and are more aligned with the applied field. It has been previously suggested that the interaction between the external electric field and the induced dipole moment of a SWNT is the driving force for the alignment.¹³ To further demonstrate the effect of electric fields, we also prepared samples with gaps at a 45° angle relative to the applied field direction. As illustrated in Fig. 2(d), most of the SWNTs are now aligned to the new electric field direction, although there are still some SWNTs in the perpendicular direction, which is due to the competing driving forces as described previously (Van der Waals interactions and thermal vibrations). It should be clear from these results that orientational growth can be programmed to obtain structures that contain crossed nanotubes, which could be very important as device structures.

Finally, we show that the growth strategy can be applied to obtain SWNTs directly on metal electrodes with good

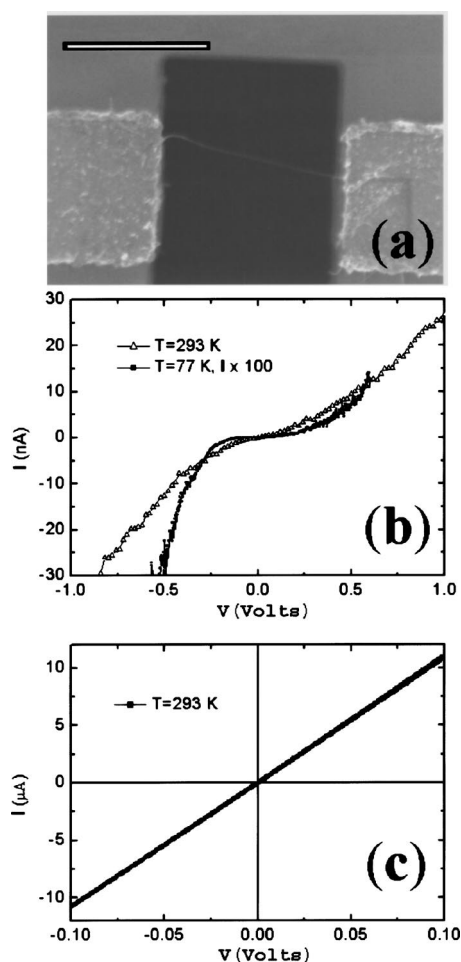


FIG. 3. (a) A suspended SWNT connecting 2 μm wide metal electrodes (Pt 50 nm/Cr 50 nm), across a gap etched all the way through the Si_3N_4 membrane. Scale bar: 2 μm . (b) I vs V curves for a sample with suspended semiconducting SWNTs at temperatures of $T=293$ K (triangles) and $T=77$ K (squares). The current (I) values for $T=77$ K are multiplied by a factor of 100. (c) I - V curve for a sample with metallic SWNTs at room temperature.

electrical contact. Two 2 μm wide electrodes (Pt 50 nm/Cr 50 nm) with Fe catalyst on top, spaced apart end on with a ~ 2 μm gap between them, were lithographically patterned in the center of Si_3N_4 membrane. A FIB was used to mill the gaps between the electrodes all the way through the Si_3N_4 membranes. CVD nanotube growth was carried out from 2 to 5 min in a methane flow of 200 sccm at 900 $^\circ\text{C}$, which usually yields only one or a few suspended SWNTs across the gaps between electrodes. Figure 3(a) shows a typical sample with a SWNT bridging an electrode gap. With this growth condition, amorphous carbon deposition on the substrate makes no contribution to the measured nanotube electrical properties. All the electrical measurement were made on the as-grown samples, without any postgrowth contacting process. Figure 3(b) shows the I - V curves for a semiconducting SWNT. At room temperature, the low-bias differential resistance is ~ 100 M Ω , and band gap-related nonlinearity is already visible. An asymmetry appears which is most likely due to contact difference at the two ends of the tube. When the temperature is reduced to 77 K, a gap is clearly observed in the I - V curve. Figure 3(c) shows the room tem-

perature I - V curve of a sample with metallic SWNTs. The linear resistance for this metallic sample is ~ 10 k Ω .

In summary, ordered SWNT arrays were grown by thermal CVD from patterned vapor deposited Fe catalysts on different substrates. External electric fields were shown to be effective in manipulating the orientation of SWNTs during the growth process despite competing tendencies. SWNT circuits with electrical contacts were constructed using the method, which may be useful in practical electronic device fabrication strategies. The controlled growth, and incorporation, of nanotubes in different geometries is important for applications in electronic, mechanical, and chemical devices.² For example, nanotubes across gaps in the free-standing membranes provide a good device geometry for chemical sensors. Crossed nanotubes bridged by appropriate molecules may provide true single molecule negative differential resistance device capabilities.¹⁴ We note that our growth strategy is highly compatible with, and adaptable to, standard semiconductor lithography processing techniques. It may therefore be important for the adoption of carbon nanotubes in future large scale practical applications which will most likely require integration with silicon based technology.

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